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THE OCCURRENCE OF ORGANOHALIDES IN CHLORINATED DRINKING WATERS

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During the course of the development of an analytical method for the determination of volatile organic solvents in water, it was observed that chloroform and other trihalogenated methanes consistently occur in drinking waters. Water supplies originating from both surface and ground water sources contain these compounds. Investigations reported here show that these compounds result from the water treatment practice of chlorination. They further show that drinking waters having surface water as their source contained higher concentrations of these compounds than those having ground water as their source. The maximum concentrations found were: chloroform - 150 µg/1, bromodichloromethane - 20 µg/1, and dibromochloromethane - 2 µg/1. Application of the method to a sewage treatment plant influent and effluent showed the presence of several other chlorinated aliphatic and aromatic compounds. (See also W75-03043)(EPA)

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THE OCCURRENCE OF ORGANOHALIDES IN CHLORINATED DRINKING WATERS

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Methods Development and Quality

Assurance Research Laboratory

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NATIONAL ENVIRONMENTAL RESEARCH CENTER
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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

The investigation reported herein was made possible by the development of a new technique for concentration and determination of volatile organic compounds in water. This technique is the subject of an Environmental Protection Agency Research Report (EPA 670/4-74-009). Using this technique it was possible to quantitate and to identify the source of chloroform and other trihalogenated methanes occurring in chlorinated drinking waters. As a result of this report and the potential chronic toxic or carcinogenic nature of these and other volatile organics, our Water Supply Research Laboratory is conducting intensive studies of the occurrence of these and other organic compounds in water supplies.

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Director
National Environmental
Research Center, Cincinnati

ABSTRACT

During the course of the development of an analytical method for the determination of volatile organic solvents in water, it was observed that chloroform and other trihalogenated methanes, consistently occur in drinking waters. Water supplies originating from both surface and ground water sources contain these compounds. Investigations reported here show that these compounds result from the water treatment practice of chlorination. They further show that drinking waters having surface water as their source contained higher concentrations of these compounds than those having ground water as their source. The maximum concentrations found were: chloroform - 150 µg/l, bromodichloromethane - 20 µg/l, and dibromochloromethane - 2 µg/l.

Application of the method to a sewage treatment plant influent and effluent showed the presence of several other chlorinated aliphatic and aromatic compounds.

ACKNOWLEDGMENT

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CONCLUSIONS

Chloroform and other trihalogenated methanes have been detected in several municipal water supplies. The highest concentrations (37 to 150 µg/l) of these compounds were found in finished waters having surface waters as their source. These compounds form as a result of chlorination processes during water treatment. The repeated addition of chlorine at various stages of the treatment process plays an important role in determining the ultimate concentrations of organohalogens that occur, since a primary limiting factor is the presence of free chlorine in the water.

Although the trihalogenated compounds resulting from chlorination are not an acute hazard to man at the levels detected [oral lethal dose of chloroform to mice is 120 mg/Kg (1)], their presence suggests the need to monitor finished waters for these and other organohalogens and to determine whether there may be chronic effects. There is a need to develop analytical methodology so that the chemistry of the chlorination process can be fully studied and understood.

In addition to chloroform, several other halogenated aliphatic and aromatic compounds were detected in a sewage treatment plant influent and effluent waters.

INTRODUCTION

In recent years there has been great speculation and concern about the effect of chlorination upon organic materials contained in natural and waste waters. Considering the widespread use of chlorine in water and sewage treatment processes, household and commercial laundering, paper pulp bleaching, and related processes, it is easy to postulate the possible inadvertent widespread production of chlorinated organic materials. There are an infinite number of organic materials commonly contained in natural and waste waters that may react with free chlorine. For the most part, mechanisms for these reactions have not been studied because rapid and precise analytical methods capable of monitoring the reaction products have not been available. Many researchers have reported the presence of organohalides in finished waters (2-7), but due to the nature of the studies made and/or the methods used, no conclusions could be drawn as to their source.

Recently, the Methods Development and Quality Assurance Laboratory of the National Environmental Research Center-Cincinnati has developed and reported on a procedure for isolating and measuring nanogram quantities of volatile and semi-volatile organic materials in waste water (8). Preliminary observations, made while developing this technique, showed the presence of organochlorine compounds in laboratory distilled and tap water. Further observations also indicated the presence of some brominated hydrocarbons in the tap waters. Raw river water, the source of the tap water, contained none or much lower concentrations of the organohalides. Since their presence in water may represent a possible health hazard and reflect a background level for industrial effluents, it was decided to quantitate and to attempt to identify the source of these compounds.

EXPERIMENTAL

Apparatus

A Perkin-Elmer 900 Gas Chromatograph was equipped with a dual-flame ionization detector and a microcoulometric detector (halide mode). Dual, stainless steel columns, 180 cm (6 ft) long X 2.67 mm (0.105 in) ID were packed with Chromosorb-101 (60/80 mesh). The oven temperature was isothermal at 190°C or programmed from 150°C to 270°C at 6.5°C/min. Nitrogen, at 50 ml/min, was employed as the carrier gas.

A Varian Aerograph 1400 gas chromatograph with a Finnigan 1015C Quadrupole Mass Spectrometer controlled by a Systems Industries 150 Data Acquisition System was employed. The glass column, 240 cm (8 ft) long X 2 mm (0.078 in) ID, was packed with Chromosorb-101 (50/60 mesh). Helium, at 30 ml/min, was employed as the carrier gas. The initial oven temperature of 125°C, was held for 3 min, and then programmed to 220°C at 4°C/min.

The purging device, trap, and desorption system used for this work have been described previously (8).

Reagents

Water free of interfering organics was prepared by passing distilled water through a Millipore Super-Q water treatment system.

Standard stock solutions were prepared by injecting 1 to 5 µl of the compound to be determined into a 1-liter volumetric flask partially filled with organic-free water. The mixture was then diluted to volume with organic-free water to give concentrations between 1 and 7 mg/l. Dilutions were then made from the stock solution by pipetting a known quantity of stock solution into a partially filled volumetric flask and diluting to volume with organic-free water. [For low level work (1 to 10 µg/l), a 1:10 dilution of the stock solution was prepared and secondary dilutions were prepared from this solution as required.]

Procedure

Water samples were collected in 125- or 500-ml, ground-glass, stoppered bottles. The bottles were carefully filled; no bubbles were allowed to pass through the samples as the bottle filled. Care was taken to eliminate the air space above the sample by over filling the bottle, then displacing part of the sample with the glass stopper. Analyses were performed as soon as possible after the sample collection. Time lapsed between collection and analyses was noted.

The water samples were analyzed for volatile components by the following procedure. Nitrogen (200 ml at 10 to 15 ml/min) was bubbled through 5.0 ml of sample to transfer the volatiles from the aqueous phase to the gaseous phase. The organic materials contained in the gaseous phase were concentrated by using a noncryogenic trapping technique (9-10) followed by a gas chromatographic analysis. This procedure (8) provides a method capable of analyzing for organic materials that are less than 2% soluble in water and that boil below 150°C. An average detection limit of 1 µg/l was achieved.

Tentative qualitative identifications were made by microcoulometric gas chromatography (MCT) and then confirmed by gas chromatography -- mass spectrographic (GC-MS) techniques. Structure determinations were verified with the use of a conversational mass spectral retrieval system (11). Quantitative data were generated with the use of the flame ionization (FID) and MCT detectors.

Standard solutions of chloroform were prepared in "organic free" distilled water at concentrations similar to those found in the unknowns. The standards and unknowns were analyzed in an identical manner, and peak areas were measured and compared for quantitative determination. At the time of analysis, reagent grade bromodichloromethane and dibromochloromethane were not available in the laboratory. Since the FID and the MCT should respond, quantatively, in an identical manner to all of these trihalogenated methane compounds (12,13) quantitative values were generated using the peak area

response of chloroform.

Samples were collected from several sources for this study. A major surface stream, a municipal water treatment plant, finished tap water from widespread locations, and a sewage treatment plant.

RESULTS AND DISCUSSION

Initial gas chromatographic analyses were performed upon the laboratory tap water with the use of the FID and MCT. Subsequently, the samples were analyzed by GC-MS to verify the identity of the compounds detected in the finished waters. The GC-MS reconstructed chromatogram and the identified components are shown in Figure 1. Unequivocal qualitative identifications of ethyl alcohol, chloroform, bromodichloromethane, and dibromochloromethane were made with the use of this instrumentation. The FID-GC was calibrated for the trihalogenated methane compounds. Although the presence of ethyl alcohol was verified by the mass spectrometer, no quantitative data was obtained.

As a matter of interest, analyses were performed upon other finished waters. Table I lists the organohalide content found in chlorinated drinking waters from several raw water sources. Where the water source was low in total organics, such as well water (approximately 0.5 mg/l of total organic carbon), the resulting concentrations of halogenated products were low. Where the water source was high in total organics, such as surface waters (5 to 10 mg/l of total organic carbon), the resulting concentrations of halogenated products were high.

Several samples were collected from various parts of a water treatment plant in a progressive manner identical to the path of the water as it is processed through the plant. See Figure 2. Table II shows the quantitative data obtained from these samples.

Large amounts of chloroform are stored and used in our laboratory. To determine whether or not accidental contamination of the samples was occurring in the laboratory, several analyses were performed upon the raw river water. These analyses were made, throughout the day, alternately with the analyses of the samples from the water treatment plant (Table II). The raw river water concentrations averaged 0.9 ± 0.2 µg/l. Based on these results, little or no contamination of the samples occurred in the laboratory.

The data reported in Table II show that the trihalogenated methanes originate at the water treatment plant. It is interesting to note that each time additional chlorine is added to maintain or increase the free chlorine concentration of the water, a significant increase in the chloroform level results. See Figure 2. The decrease in the concentration of trihalogenated methanes after sampling point 4 may be due to the introduction of an activated carbon slurry at that point.

A second series of analyses were performed upon raw river water which had been treated with alum and chlorine. The sample was collected at the water treatment plant and held in the laboratory for 71 hours. It was analyzed five times within the first 6 hours. After standing overnight, it

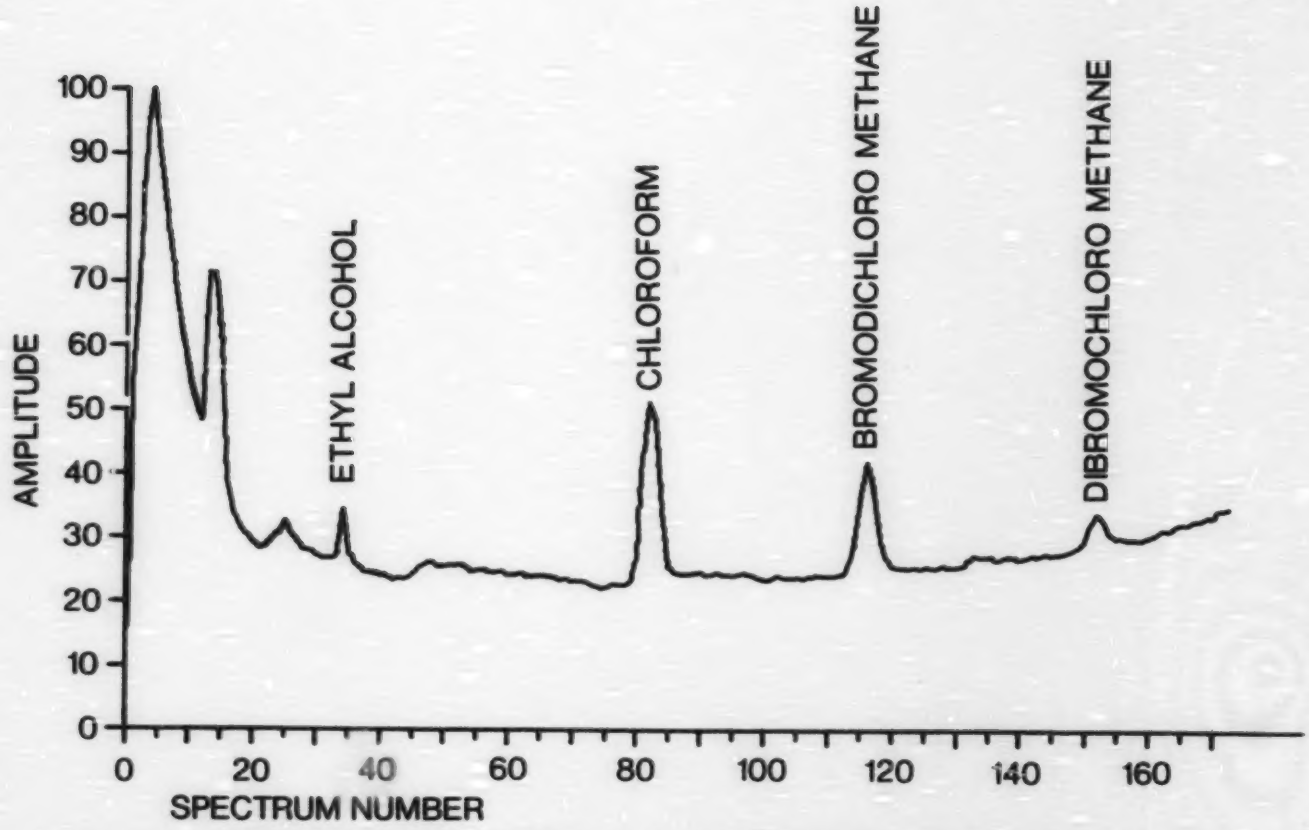

Figure 1. RECONSTRUCTED GC-MS CHROMATOGRAM OF FINISHED WATER.

Table I. TRIHALOGENATED METHANE CONTENT OF VARIOUS MUNICIPAL WATER SUPPLIES

Sampling Sites	Raw water source	Date collected	Concentration (µg/l)		
			Chloroform	Bromo-dichloro-methane	Dibromo chloro-methane
100[a]	Surface	8-73	94.0	20.8	2.0
100[a]	Surface	2-74	37.3	9.1	1.3
101[b]	Surface	2-74	70.3	10.2	0.4[c]
102[b]	Surface	2-74	152.0	6.2	0.9[c]
103[b]	Surface	2-74	84.0	2.9	<0.1
104[a]	Well	8-73	2.9	No data	No data
104[a]	Well	2-74	4.4	1.9	0.9[c]
105[a]	Well	2-74	1.7	1.1	0.8[c]
106[b]	Well	12-73	3.5	No data	No data

[a]Sample age <4 hours.

[b]Sample age unknown; >24 hours.

[c]Approximate value, ±20%.

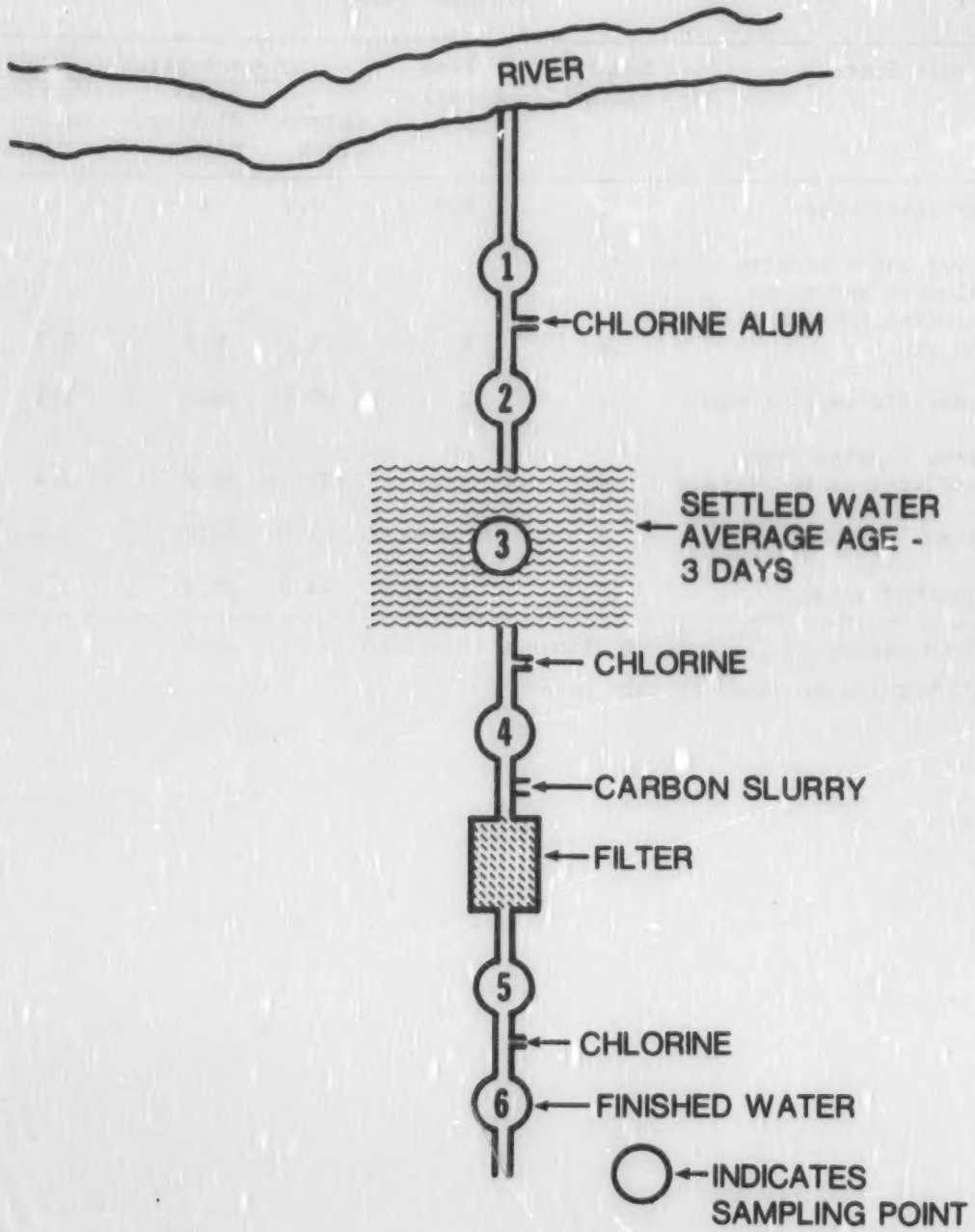

Figure 2. WATER TREATMENT PLANT SAMPLING POINTS

Table II. TRIHALOGENATED METHANE CONTENT OF WATER FROM WATER TREATMENT PLANT

Sample Source	Sampling point	Free chlorine ppm	Concentration (μg/l)		
			Chloroform	Bromo dichloromethane	Dibromochloromethane
Raw river water	1	0.0	0.9	a	a
River water treated with chlorine and alum-chlorine contact time ~80 min.	2	6	22.1	6.3	0.7
3-day-old settled water	3	2	60.8	18.0	1.1
Water flowing from settled area to filters[b]	4	2.2	127	21.9	2.4
Filter effluent	5	Unknown	83.9	18.0	1.7
Finished water	6	1.75	94.0	20.8	2.0

[a] None detected. If present, the concentration is <0.1 μg/l.

[b] Carbon slurry added at this point.

was analyzed at 26, 28, 29 and 71 hours. In Figure 3 can be seen the concentrations of halogenated methanes found. These data show that in this static system, after a single addition of free chlorine, trihalogenated methane compounds are formed. Their concentration increased with respect to chlorine contact time up to approximately 15 hours. Little or no increase was noted after that time. This observation and the previous observation that each addition of free chlorine produces an increase in the concentration of trihalogenated methanes show that these compounds are not introduced as impurities contained in the alum or the chlorine used for treatment of the water. It is apparent that a chemical reaction is taking place between free chlorine and organic compounds present in the water. One possible mechanism for the formation of chloroform is suggested by the compounds detected in the tap water -- ethanol and trihalogenated methanes only (no mono- or dihalogenated compounds). The ethanol oxidizes to acetaldehyde that reacts with free chlorine to form chloral. The chloral reacts with water to form chloral hydrate which then decomposes to form chloroform.

$$CH_3\text{-}CH_2OH \longrightarrow CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}H \longrightarrow Cl_3\text{-}C\text{-}\overset{O}{\overset{\|}{C}}\text{-}H \longrightarrow Cl_3\text{-}C\text{-}\overset{H}{\overset{|}{C}}\text{-}(OH)_2 \longrightarrow CHCl_3$$

At this time, we have no experimental evidence to show that this is in fact the mechanism by which the chloroform is produced.

The presence of the two brominated compounds listed in Table I probably results from bromine impurities contained in the chlorine. The bromine would react in the same manner as chlorine to form the brominated homologs. The concentration of the tribrominated homolog, bromoform, if present, was below the detection limit of the method. Other researchers (2) have reported the presence of these trihalogenated compounds, including bromoform, in finished waters, but the possibility that they may have resulted from the chlorination process was not suggested.

Table III lists results of the analyses of grab samples collected at several stages of treatment in a local sewage treatment plant. Since this treatment plant serves a large industrial as well as a municipal area, a multitude of diverse organic compounds should be present at all times. Because of the constantly changing composition of the water entering the plant, drawing any comparisons between the quantitative data for the influent water and the effluent water is difficult. The increase of the chloroform concentration in the chlorinated effluent, however, appears to be due to chlorination. The variation in the concentrations of the chlorinated compounds before and after chlorination ranged from 0.2 to 1.2 µg/l, except for chloroform which increased by 5 µg/l. This increase, while small, is well above the observed variation (±20%) of the method at its lower limit of detection. The closeness of the results for the other chlorinated compounds and the close proximity of the sampling points before and after chlorination indicate that the increase in the concentration of chloroform results from the chlorination process. Since the amount of chlorine added at the sewage treatment plant was low (0.25 ppm total chlorine) when compared with that added at the water treatment plant and since the contact

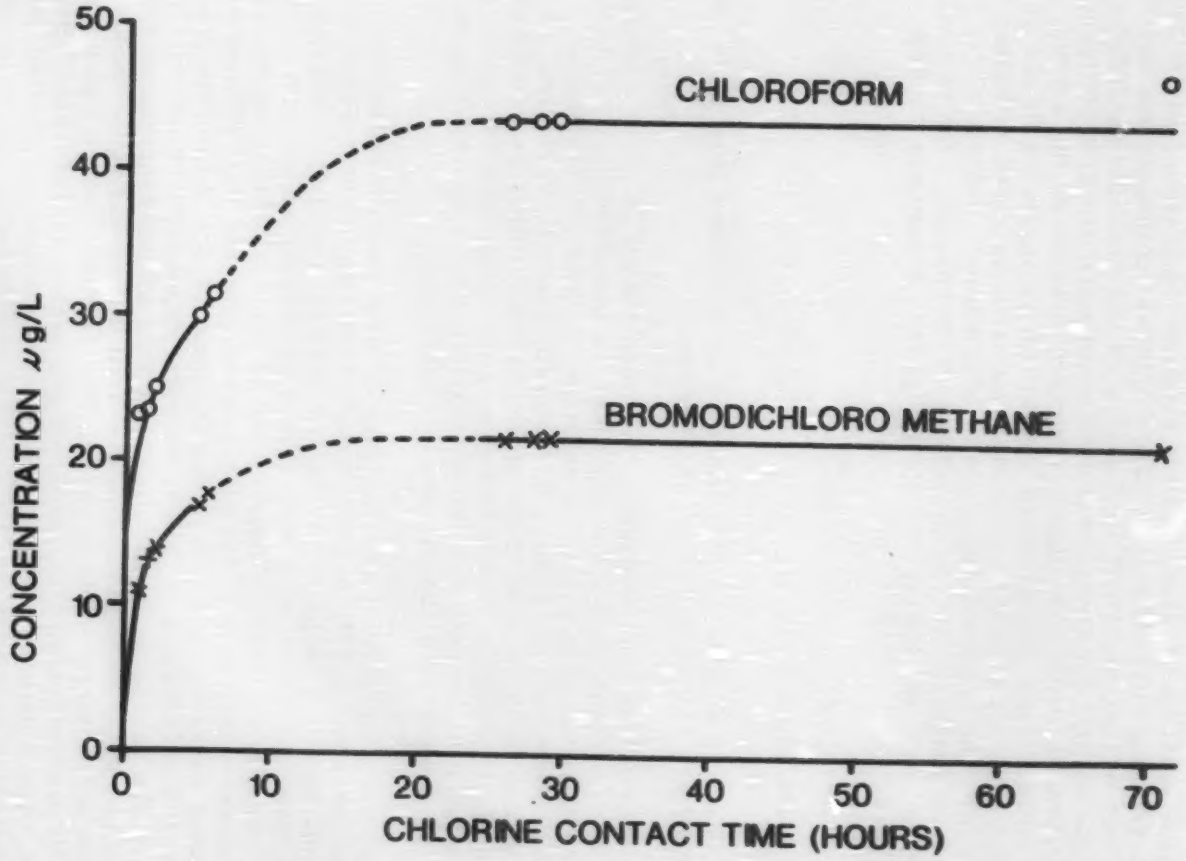

Figure 3. CHLORINATED OHIO RIVER WATER.

time between collection and analysis was less than 2 hours, the low concentration of chloroform is not surprising.

Table III. ORGANOCHLORINE COMPOUNDS IN WATER FROM SEWAGE TREATMENT PLANT

Compound[a]	Concentration (µg/l)		
	Influent before treatment	Effluent before chlorination	Effluent after chlorination
Methylene chloride	8.2	2.9	3.4
Chloroform	9.3	7.1	12.1
1,1,1-Trichloroethane	16.5	9.0	8.5
1,1,2-Trichloroethylene	40.4	8.6	9.8
1,1,2,2-Tetrachloroethylene	6.2	3.9	4.2
Σ Dichlorobenzenes	10.6	5.6	6.3
Σ Trichlorobenzenes	66.9	56.7	56.9

[a]All confirmed by GC-MS

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